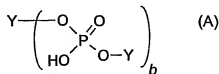


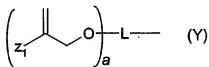
Claims

1. One-part self-etching, self-priming dental adhesive composition having a pH of at most 2, which comprises
- (a) a polymerizable acidic phosphoric acid ester monomer of the following formula (A):



wherein

the moieties Y independent from each other represent a hydrogen atom or a moiety of the following formula (Y)



wherein

Z_1 is COOR^{10} , COSR^{20} , $\text{CON}(\text{R}^{10})_2$, $\text{CONR}^{10}\text{R}^{20}$, or CONHR^{10} , wherein R^{10} and R^{20} independently represent

a hydrogen atom,
 a C_{1-18} alkyl group optionally substituted by a C_{3-8} cycloalkyl group,
 an optionally substituted C_{3-8} cycloalkyl group,
 an optionally substituted C_{6-18} aryl or heteroaryl group,
 an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, or
 an optionally substituted C_{7-30} aralkyl group,
 whereby two R_1 residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,
 and whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-5} alkyl group(s);

L represents an $(a+b)$ -valent organic residue (whereby b is 1 when Y in

formula (A) is within the round brackets) containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including $a + b$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $a + b$ carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;

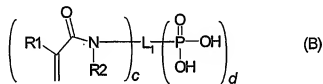
a is an integer of from 1 to 10, preferably 1 to 5;

b is an integer of from 1 to 10, preferably 1 to 5;

provided that at least one Y is not hydrogen; and

(b) one or more polymerisable acidic monomers selected from the group consisting of

(b1) polymerisable acidic monomers of the following formula (B):



wherein

R_1 and R_2 independently represent

a hydrogen atom,

an optionally substituted C_{1-18} alkyl group,

an optionally substituted C_{3-18} cycloalkyl group,

an optionally substituted C_{5-18} aryl or heteroaryl group,

an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group,

an optionally substituted C_{7-30} aralkyl group,

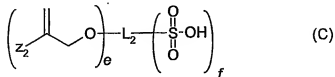
whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-5} alkyl group(s);

L_1 represents a $(c + d)$ valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur, the carbon atoms including $c + d$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $c + d$ carbon atoms linking a phosphonate or optionally substituted acrylamido group;

and

c and d independently represent integers of from 1 to 10;

(b2) polymerisable acidic monomers of the following formula (C):

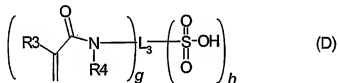


wherein

Z₂ independently has the same meaning as defined for Z₁;

L₂ represents an (e + f) valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including e + f carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said e + f carbon atoms linking a sulphonate or optionally substituted 2-(oxa-ethyl)acryl derivative group; and e and f independently represent an integer of from 1 to 10;

(b3) acidic monomers of the following formula (D):



wherein

R₃ and R₄ independently represent

a hydrogen atom,

an optionally substituted C₁₋₁₈ alkyl group,

an optionally substituted C₃₋₁₈ cycloalkyl group,

an optionally substituted C₆₋₁₈ aryl or heteroaryl group,

an optionally substituted C₆₋₁₈ alkylaryl or alkylheteroaryl group,

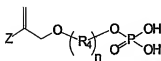
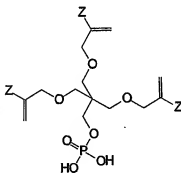
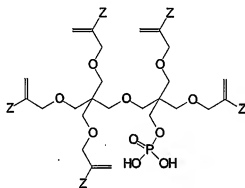
an optionally substituted C₇₋₃₀ aralkyl group,

whereby the optionally substituted groups may be substituted by 1 to 5 C₁₋₅ alkyl group(s)

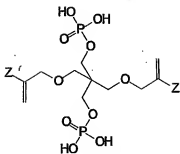
L_3 represents a $(g + h)$ valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including $g + h$ carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said $g+h$ carbon atoms linking a sulphonate or optionally substituted acrylamido group; and g and h independently represent integers of from 1 to 10;

- (c) a polymerizable N-substituted alkylacrylic or acrylic acid amide monomer;
 - (d) optionally an organic and/or inorganic acid;
 - (e) an organic water soluble solvent and/or water; and
 - (f) polymerization initiator, inhibitor and stabilizer.
2. The one-part self-etching, self-priming dental adhesive composition of claim 1 wherein L_1 , L_2 , and L_3 independently represent an optionally substituted C_{1-18} alkylene group which may contain from 1 to 9 oxygen atoms in the chain, an optionally substituted C_{3-18} cycloalkylene group, an optionally substituted C_{6-18} arylene or heteroarylene group, an optionally substituted C_{6-18} alkylaryl or alkylheteroarylene group, an optionally substituted C_{7-30} aralkylene group.
3. The one-part self-etching, self-priming dental adhesive composition of claim 1 which is hydrolysis stable for at least one week at a storage temperature of 50 °C, whereby after such storage the bond strength of an adhesive prepared from such an adhesive composition to enamel and/or dentin is at least 10 MPa, preferably 15 MPa.
4. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein components (a) and (b) are contained in a ratio of from 1:100 to 100 : 1.
5. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein said organic acid of component (d) is selected from the group of mono- or polycarboxylic acids such as methacrylic acid, acrylic acid, fumaric acid, maleic acid, citric acid, itaconic acid, formic acid and wherein the inorganic acid of component (d) is selected from the group of sulfonic acid, phosphoric acid, sulfuric acid and hydrofluoric acid.

6. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein said organic water soluble solvent of component (e) is selected from the group of alcohols and ketones such as ethanol, propanol, butanol, acetone, methyl ethyl ketone.
7. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein said acidic polymerizable monomer of component (a) is characterized by one of the following formulas:

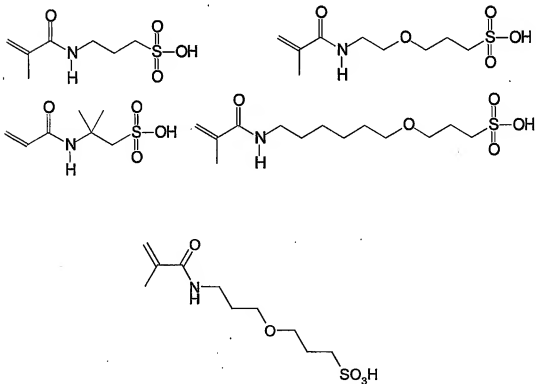


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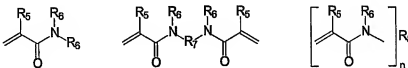


wherein Z is as defined in claim 1 and
n is an integer.

8. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein said acidic polymerizable monomer of component (b) is a polymerisable acidic monomers of formula (C).
9. Hydrolysis stable one-part self-etching, self-priming dental adhesive composition of claim 8, wherein said acidic polymerizable monomer is characterized by one of the following formulas:



10. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein the polymerizable N-substituted alkylacrylic or acrylic acid amide monomer of component (c) is characterized by one of the following formulas:



wherein

R_5 and R_6 independently represent

a hydrogen atom or a substituted

a C_1 to C_{18} alkyl group,

an optionally substituted C_3 - C_{18} cycloalkyl group,

an optionally substituted C_5 - C_{18} aryl or heteroaryl group,

an optionally substituted C_6 - C_{18} alkylaryl or alkylheteroaryl group,

an optionally substituted C_7 - C_{30} aralkyl group,

R_7 represents a

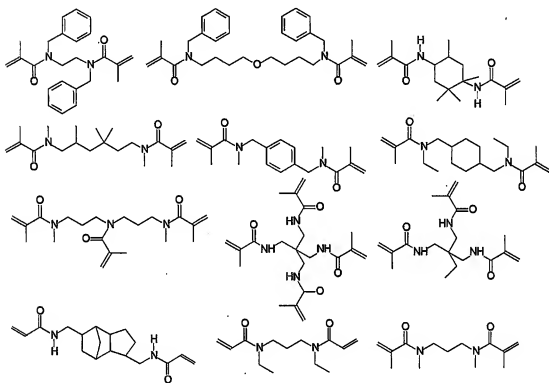
a divalent substituted or unsubstituted organic residue having from 1 to 45 carbon atoms, whereby said organic residue may contain from 1 to 14 oxygen and/or nitrogen atoms and is selected from a C_1 to C_{18} alkylene group wherein from 1 to 6 $-CH_2$ -groups may be replaced by a $-N-(C=O)-CR_9=CH_2$ group wherein R_9 is a hydrogen atom or a C_1 to C_{18} alkyl group, a divalent substituted or unsubstituted C_3 to C_{18} cycloalkyl or cycloalkylene group, a divalent substituted or unsubstituted C_4 to C_{18} aryl or heteroaryl group, a divalent substituted or unsubstituted C_5 to C_{18} alkylaryl or alkylheteroaryl group, a divalent substituted or unsubstituted C_7 to C_{30} aralkyl group, and a divalent substituted or unsubstituted C_2 to C_{45} mono-, di- or polyether group having from 1 to 14 oxygen atoms,

R_9 represents

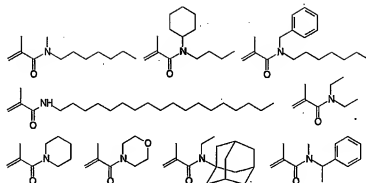
a saturated di- or multivalent substituted or unsubstituted C_2 to C_{18} hydrocarbon group, a saturated di- or multivalent substituted or unsubstituted cyclic C_3 to C_{18} hydrocarbon group, a di- or multivalent substituted or unsubstituted C_4 to C_{18} aryl or heteroaryl group, a di- or multivalent substituted or unsubstituted C_5 to C_{18} alkylaryl or alkylheteroaryl group, a di- or multivalent substituted or unsubstituted C_7 to C_{30} aralkyl group, or a di- or multivalent substituted or unsubstituted C_2 to C_{45} mono-, di-, or polyether residue having

from 1 to 14 oxygen atoms, and
n is an integer.

11. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein said polymerizable monomer is a mono-, bis- or poly(meth) acrylamide characterized by one of the following formulas:



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12. The one-part self-etching, self-priming dental adhesive composition according to claim 1, which contains said acidic polymerizable monomers of components (a) and (b) in an amount of from 5 to 90 wt-%.
13. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein said polymerization initiator is a thermal initiator, a redox-initiator or a photo initiator.
14. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein said photo initiator is champhor quinone.
15. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein said filler is an inorganic filler and/or an organic filler; preferably the filler is a nanofiller.
16. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein said stabilizer is a radical absorbing monomer such as hydroquinone, hydroquinone monomethylether, 2,6-di-tert.-butyl-p-cresol.
17. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein L represents
 - an (a+b)-valent saturated aliphatic C₂ to C₁₈ group having at least 2 of said primary aliphatic carbon atoms, and optionally 1 or more of said secondary aliphatic carbon atom(s), whereby said (a+b)-valent group may be substituted by C₁ to C₈ alkyl group(s); or
 - a C₂ to C₄₈ mono-, di-, or polyether which has from 1 to 14 oxygen atoms and

is substituted by at least 2 C₁ to C₁₀ aliphatic group(s) having said primary and/or secondary aliphatic carbon atoms; whereby said ether may optionally be substituted by C₁ to C₅ alkyl group(s); or

wherein L represents:

a saturated C₃ to C₈ cyclic, C₇ to C₁₅ bi- or polycyclic hydrocarbon group having from 0 to 4, preferably, 0 to 3, more preferably 0 or 1, of said secondary alicyclic carbon atoms; and/or

a C₄ to C₁₈ aryl or heteroaryl group having from 0 to 5, preferably 0 to 3, more preferably 0 or 1, of said aromatic carbon atoms; whereby said saturated hydrocarbon or aryl or heteroaryl group is substituted by

from 0 to 5 C₁ to C₅ alkyl group(s);

from 0 to 4, preferably 1 to 3, more preferably 1 or 2, saturated C₁ to C₁₀ aliphatic group(s) having said primary and/or secondary aliphatic carbon atoms, and/or

from 0 to 2 divalent residues according to one of the following formulas:

-[O-CH₂CH₂]_f- wherein f is an integer of from 1 to 10, preferably 1 to 5;

-[O-CH₂CH₂CH₂]_g- wherein g is an integer of from 1 to 10, preferably 1 to 5;

-[O-R₁₂]_h- wherein R₁₂ is -CH(CH₃)-CH₂- or -CH₂-CH(CH₃)- and h is an integer of from 1 to 10, preferably 1 to 5;

-[O-R₁₄]_i-[O-R₁₅]_j- or -[O-R_{15k}]-[O-R₁₄]_l- wherein R₁₄ is -CH₂CH₂-, R₁₅ is -CH(CH₃)-CH₂- or -CH₂-CH(CH₃)-, i, j, k, and l are integers whereby 2i + 3j ≤ 15 and 2k + 3l ≤ 15,

-[O-CH₂CH₂CH₂CH₂]_r- wherein r is an integer of 1 or 2;

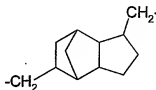
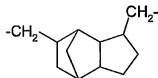
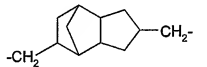
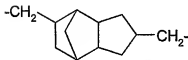
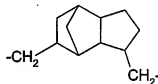
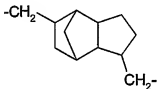
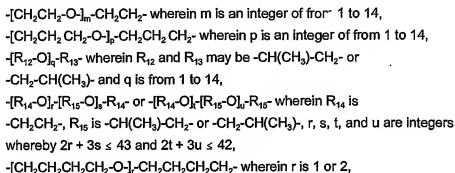
wherein said divalent residues have one of said primary aliphatic carbon atoms; and

whereby 2 groups selected from said saturated hydrocarbon, aryl, and heteroaryl groups may optionally be linked by a single bond, an alkylene group, or -O-.

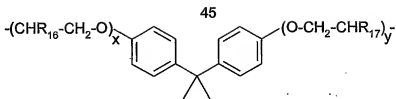
18. The one-part self-etching, self-priming dental adhesive composition according to claim 1,
- wherein L represents
- an (a+b)-valent saturated C₃ to C₈ cyclic or C₇ to C₁₅ bi- or tricyclic hydrocarbon group having at least 2 of said secondary alicyclic carbon atoms;
- an (a+b)-valent saturated C₄ to C₁₈ aryl or heteroaryl group having from 2 to 6 of said aromatic carbon atoms;
- an (a+b)-valent C₆ to C₁₈ alkylaryl or alkyl heteroaryl group having at least one of said aromatic carbon atoms, at least one of said secondary aliphatic carbon atoms, and

optionally one of said primary aliphatic carbon atoms at the terminal end of the alkyl moiety of said alkylaryl or alkylheteroaryl group; or
 an (a+b)-valent C₆ to C₃₀ aralkyl group having at least one of said primary aliphatic carbon atoms and at least one of said secondary aliphatic carbon atoms.

19. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein L represents is a divalent residue according to one of the following formulas:

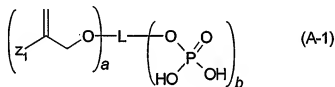


or



wherein R_{16} and R_{17} are H or $-\text{CH}_3$ and x and y may independently be integers of from 0 to 10, preferably 0 to 5.

20. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein said $(a+b)$ carbon atoms are primary aliphatic carbon atoms.
21. The one-part self-etching, self-priming dental adhesive composition according to claim 1, wherein the polymerizable acidic phosphoric acid ester monomer is of the following formula (A-1):



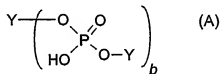
wherein

Z_1 is COOR^{10} , COSR^{20} , $\text{CON}(\text{R}^{10})_2$, $\text{CONR}^{10}\text{R}^{20}$, or CONHR^{10} , wherein R^{10} and R^{20} independently represent

a hydrogen atom,
 a C_{1-18} alkyl group optionally substituted by a C_{3-8} cycloalkyl group,
 an optionally substituted C_{3-8} cycloalkyl group,
 an optionally substituted C_{4-18} aryl or heteroaryl group,
 an optionally substituted C_{5-18} alkylaryl or alkylheteroaryl group, or
 an optionally substituted C_{7-30} aralkyl group,
 whereby two R_1 residues may form together with the adjacent nitrogen atom to which they are bound a 5- to 7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,
 and whereby the optionally substituted groups may be substituted by 1 to 5 C_{1-3} alkyl group(s);

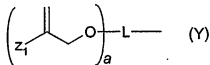
L represents an (a+b)-valent organic residue containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including a + b carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said a+b carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;
 a is an integer of from 1 to 10, preferably 1 to 5;
 b is an integer of from 1 to 10, preferably 1 to 5.

22. The one-part self-etching, self-priming dental adhesive composition according to claim 1 wherein none of the moieties Y is a hydrogen atom.
23. A polymerizable acidic phosphoric acid ester monomer of the following formula (A)



wherein

the moieties Y independent from each other represent
 a moiety of the following formula (Y)



wherein

Z₁ is COOR¹⁰, COSR²⁰, CON(R¹⁰)₂, CONR¹⁰R²⁰, or CONHR¹⁰, wherein

R¹⁰ and R²⁰ independently represent

a hydrogen atom,

a C₁₋₁₈ alkyl group optionally substituted by a C₃₋₈ cycloalkyl group,

an optionally substituted C₃₋₈ cycloalkyl group,

an optionally substituted C₄₋₁₈ aryl or heteroaryl group,

an optionally substituted C₅₋₁₈ alkylaryl or alkylheteroaryl group, or

an optionally substituted C₇₋₃₀ aralkyl group,

whereby two R_i residues may form together with the adjacent nitrogen atom to which they are bound a 5- to

7-membered heterocyclic ring which may contain further nitrogen atoms or an oxygen atoms,
and whereby the optionally substituted groups may be substituted by 1 to 5 C₁₋₆ alkyl group(s);

L represents an (a+b)-valent organic residue (whereby b is 1 when Y in formula (A) is within the round brackets) containing 2 to 45 carbon atoms and optionally heteroatoms such as oxygen, nitrogen and sulfur atoms, the carbon atoms including a + b carbon atoms selected from primary and secondary aliphatic carbon atoms, secondary alicyclic carbon atoms, and aromatic carbon atoms, each of said a+b carbon atoms linking a phosphate or 2-(oxa-ethyl)acryl derivative group;
a is an integer of from 1 to 10, preferably 1 to 5;
b is an integer of from 1 to 10, preferably 1 to 5, more preferably 1.